Inhibition of Electrochemical Reactions at Gold Surfaces by Grafted, Highly Fluorinated, Hyperbranched Polymer Films

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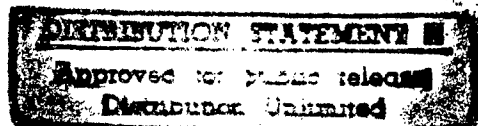David E. Bergbreiter,*[1] and Richard M. Crooks*[2]

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13. ABSTRACT (Maximum 200 words)

We report the synthesis and passivation properties of surface-grafted, highly fluorinated, hyperbranched poly(acrylic acid) (PAA) films that contain 50 atom% F. These films are very hydrophobic (water contact angle of 114°) and block electrochemical reactions on gold electrodes. Cyclic voltammetry in basic solution shows that while an electrode covered with a 3-layer PAA (3-PAA) film mimics an assembly of microelectrodes, a fluorinated 3-layer PAA (3-PAA/F) film blocks nearly all electron transfer to the gold surface. The charge transfer resistance of electrodes covered with a 3-PAA/F film is about 40 times greater than that for an electrode covered with a nonfluorinated 3-PAA film. 3-PAA/F films are initially 10 times more blocking than $C_{16}SH$ SAMs. Additionally, while the SAM is desorbed by electrochemical cycling, 3-PAA/F films are still highly blocking after ten potential sweeps over a 1.5 V range. Thus fluorinated PAA films are promising candidates for corrosion-inhibiting coatings.

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Abstract

We report the synthesis and passivation properties of surface-grafted, highly fluorinated, hyperbranched poly(acrylic acid) (PAA) films that contain 50 atom% F. These films are very hydrophobic (water contact angle of 114°) and block electrochemical reactions on gold electrodes. Cyclic voltammetry in basic solution shows that while an electrode covered with a 3-layer PAA (3-PAA) film mimics an assembly of microelectrodes, a fluorinated 3-layer PAA (3-PAA/F) film blocks nearly all electron transfer to the gold surface. The charge transfer resistance of electrodes covered with a 3-PAA/F film is about 40 times greater than that for an electrode covered with a nonfluorinated 3-PAA film. 3-PAA/F films are initially 10 times more blocking than $C_{16}SH$ SAMs. Additionally, while the SAM is desorbed by electrochemical cycling, 3-PAA/F films are still highly blocking after ten potential sweeps over a 1.5 V range. Thus fluorinated PAA films are promising candidates for corrosion-inhibiting coatings.

Introduction

Here we report that hydrophobic, highly fluorinated, hyperbranched poly(acrylic acid) (PAA) films effectively passivate metal surfaces. For example, ac-impedance measurements obtained in basic solution show that fluorinated PAA films confined to Au surfaces are about 10^4 times more effective at blocking electrochemical reactions than are the mercaptoundecanoic acid (MUA) monolayers onto which they are grafted.

To prepare PAA films, we first graft poly(*tert*-butyl acrylate) onto a Au-confined MUA monolayer. Hydrolysis of the *tert*-butyl esters then yields a PAA graft and additional grafting at multiple $-CO_2H$ sites on each prior graft leads to hyperbranched PAA films.[1] We previously demonstrated that derivatization of the $-CO_2H$ groups of PAA films with $H_2NCH_2(CF_2)_6CF_3$ yields a fluorinated film.[2,3] Now we show that a subsequent activation of unreacted $-CO_2H$ groups in a fluorinated film followed by reaction with $H_2NCH_2(CF_2)_6CF_3$ produces an even more highly fluorinated film that is quite stable and highly passivating. Interestingly, however, one fluorination step produces a slightly more passivating film than two fluorination steps.

Because corrosion is an important problem worldwide there are many strategies for corrosion inhibition including deposition of thin, passivating metal, metal oxide and organic coatings.[4,5] Thin organic films are deposited by techniques such as spraying, painting, and spin and dip coating. The development of self-assembled monolayers (SAMs) showed that even ultrathin layers of highly organized material can block electrochemical reactions and

in certain cases reduce the rate of corrosion.[6-10] SAMs are attractive because they are strongly linked to the substrate and are amenable to objects having unusual geometries as well as on-line modification where spin and dip coating are impractical. However the durability and corrosion resistance of SAMs is limited.[6-15] Alkylsiloxane polymers grafted onto alcohol-terminated SAMs provide better corrosion resistance than SAMs, but the thickness and corrosion resistance of these two-dimensional coatings are also limited.[16-18]

We are developing corrosion-resistant coatings based on hyperbranched PAA covalently linked to SAMs via simple chemical reactions. These films are structurally and chemically versatile, because they can be derivatized to yield a wide variety of chemical compositions and their thicknesses can be varied from 30 to >1000 Å. Fluorinated PAA films are much more durable and blocking than SAMs (*vide infra*) and their ability to span substrate defects should make them excellent corrosion inhibitors even on geometrically complex objects.

Experimental Section

Film Preparation. 3-layer PAA (3-PAA) films and fluorinated 3-PAA (3-PAA/F) films were prepared as described previously.[3] Mercaptoundecanoic acid (MUA) and hexadecyl mercaptan ($C_{16}SH$) SAMs on Au-coated Si(111) wafers were prepared by immersing plasma-cleaned substrates either in ethanolic 0.001 M MUA for 30 min or ethanolic 0.001 M $C_{16}SH$ for 72 h then rinsing the films with EtOH and water. To prepare grafted PAA films, the MUA SAM was

activated with isobutyl (or ethyl) chloroformate to form an anhydride intermediate. Reaction with H_2NR-PTBA-RNH_2 (R = $(CH_2)_2NHCO(CH_2)_2C(CN)(CH_3)$) and subsequent hydrolysis yields a grafted layer of PAA. Cycles of activation of the $-CO_2H$ groups of PAA with chloroformate followed by reaction with H_2NR-PTBA-RNH_2 and hydrolysis yield subsequent PAA layers. PAA films were fluorinated by activating their $-CO_2H$ groups and then allowing them to react with $H_2NCH_2(CF_2)_6CF_3$ (0.1 M in DMF). Prior to electrochemical measurements, any loosely bound material was removed from the films by immersion in 0.1 M HCl in EtOH for 5 min, sonication in $CHCl_3$ for 5 min, and rinsing in EtOH. 3-PAA/2F films were prepared by activating a cleaned 3-PAA/F film with chloroformate and again allowing it to react with $H_2NCH_2(CF_2)_6CF_3$.

Analysis. Cyclic voltammetric and ac-impedance measurements were performed in a five-necked, three-electrode cell using a Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems, West Lafayette, IN) and a Pt gauze counter electrode which was separated from the main compartment by a porous glass plug. The working electrode was cut from a Au-coated Si(111) wafer (e-beam evaporated Au (200 nm) on an adhesion layer of 5 nm Cr) and contained within a Teflon/o-ring holder that exposed an area of 0.09 cm^2. Impedance measurements were performed using an EG&G PARC 273A potentiostat and a Solartron 1255 frequency response analyzer controlled by a microcomputer running ZPLOT software (Scribner Associates, Charlottesville, VA). Measurements were performed at 5 mV (root-mean squared) around E^O (272 mV) of the $Fe(CN)_6^{4-/3-}$ couple, and impedance values were determined at five discrete

frequencies per decade. The range of frequencies applied was 0.01 Hz to 65 kHz. Results were analyzed using ZPLOT and ZSIM/CNLS software packages. Cyclic voltammetric measurements were carried out using a BAS model 100B Electrochemical Analyzer (Bioanalytical System, Inc.).

All experiments were performed in pH 9.9 buffer (0.2 M NH_4OH + 0.036 M NH_4Cl) containing 1.0 M KCl as supporting electrolyte. Solutions were purged with N_2 prior to measurements, and during ac-impedance experiments the solution was purged with N_2 at the rate of about two bubbles per second. During cyclic voltammetry experiments, N_2 was blown over the solution. X-ray photoelectron spectroscopy (XPS), Fourier transform infrared external reflection spectroscopy (FTIR-ERS), ellipsometric thickness, and contact-angle measurements were described previously.[3]

Results and Discussion

Synthesis of highly fluorinated films. We previously reported the fluorination of 3-PAA films with $H_2NCH_2(CF_2)_6CF_3$ through a single cycle of $-CO_2H$ activation and subsequent reaction with $H_2NCH_2(CF_2)_6CF_3$. XPS elemental analysis showed that the surface of these films contains 46 atom% F. Reactivation of the 3-PAA/F film followed by reaction with $H_2NCH_2(CF_2)_6CF_3$ yields a 3-PAA/2F film that contains 50 atom% F, which represents 93% of the theoretical maximum expected in a homopolymer of $(CH_2CHCONHCH_2(CF_2)_6CF_3)_n$. FTIR-ERS spectra (Figure 1) also show an increase in fluorination upon a second cycle of activation and reaction with $H_2NCH_2(CF_2)_6CF_3$. The absorbance of peaks due to CF_x

stretching modes increases by approximately 40% after a second reaction with $H_2NCH_2(CF_2)_6CF_3$. Moreover, amide peaks (1680 and 1550 cm^{-1}) arising from the coupling reaction increase after the second fluorination reaction, and the peak due to the acid carbonyl of unreacted $-CO_2H$ groups (≈ 1730 cm^{-1}) is reduced to a barely detectable shoulder. The surface energy of 3-PAA/F films also decreases after a second fluorination. Water contact angles on PAA films increase from 25° to 109° after one fluorination reaction and to 114° after a second fluorination. Taken together, the XPS, FTIR-ERS, and contact angle results confirm a highly fluorinated, low-energy film.

Impedance analysis of PAA-coated electrodes. Organic films confined to electrodes can affect charge transfer resistance (R_{ct}), interfacial capacitance, mass transport of reactants to the electrode surface, and the apparent heterogeneous rate constant for electron transfer ($k°$). Impedance analysis is a powerful tool that sometimes leads to a straightforward determination of diffusion and kinetic constants for electrochemical systems. This technique is especially well-suited for studies of thin films because the very small ac perturbation (in this case 5 mV rms) causes only minimal changes in the coverage or structure of the film.[19-21]

Figure 2 shows plots of complex impedances at many frequencies for naked, MUA-, 3-PAA-, 3-PAA/F-, and 3-PAA/2F-coated Au electrodes in a pH 9.9-buffer solution containing 5 mM $Fe(CN)_6^{3-}$ and 5 mM $Fe(CN)_6^{4-}$. The plot for naked Au reveals a barely discernible semicircle at high frequencies and a 45° line

characteristic of Warburg diffusion.[22] The dominance of the
Warburg impedance indicates that the redox reaction is diffusion-
controlled. For the MUA-covered electrode, we observe a larger-
diameter semicircle accompanying the mass transfer-limited
behavior at lower frequencies. We used Randle's equivalent
circuit to model these systems, and thus the diameter of the
semicircle is equal to R_{ct}.[21,23-25] The much larger diameter of the
semicircle for 3-PAA-, 3-PAA/F-, and 3-PAA/2F-covered electrodes
demonstrates the enhanced barrier properties of these films. As
shown in Table 1, the average R_{ct} for the 3-PAA/F film is 40 times
greater than that of the already passivating 3-PAA film and 10^4
times greater than the MUA monolayer. The 3-PAA/F film is also 10
times more blocking than a $C_{16}SH$ monolayer (Table 2), which itself
has an excellent capacity for blocking electrode reactions.[7]
Interestingly, 3-PAA/2F films are comparable or slightly worse at
blocking electrode reactions than 3-PAA/F films even though the
surfaces of 3-PAA/2F films are more hydrophobic. We think that
this results from a change in film morphology during the second
cycle of activation and reaction with $H_2NCH_2(CF_2)_6CF_3$.

    We estimated the effective fractional surface coverage (θ)
using eq 1 where R_{ct}^o is the charge transfer resistance of bare
gold.[21] This equation is derived from a pin-hole model

$$\theta = (R_{ct} - R_{ct}^o)/R_{ct} \qquad\qquad (1)$$

that is based on a heterogeneous Au surface. A fraction of the
electrode $(1-\theta)$ is composed of naked gold which is accessible to the

redox couple. Electron transfer at these sites is characterized by the k° for $Fe(CN)_6^{3-/4-}$. The remaining fraction of the electrode (θ) is assumed to be completely covered by the film and is therefore unavailable for electron transfer. Table 1 lists θ values for the different modified electrodes. Although all of the films grow from a relatively permeable MUA SAM, coverage greatly increases with the addition of 3-PAA, 3-PAA/F, and 3-PAA/2F polymer layers.

Figure 3 shows cyclic voltammetry of several film-covered electrodes in a pH 9.9-buffered aqueous solution containing 5 mM $Fe(CN)_6^{3-}$ obtained using scan rates ranging from 10 to 500 mV/s. Voltammetry of the 3-PAA/F-coated electrode consists mainly of charging current showing that this film effectively blocks electron transfer at the electrode interface. The plateau currents of the $C_{16}SH-$ and 3-PAA- coated electrodes change very little as a function of scan rate. This behavior is characteristic of radial diffusion to an assembly of noninteracting microelectrodes.[24,26] The steady-state currents of $C_{16}SH$-coated electrodes are larger than those of 3-PAA/F- and 3-PAA/2F-coated electrodes as expected from the active areas of these electrodes determined by ac-impedance analysis.[27,28]

3-PAA/F films are also more durable than $C_{16}SH$ monolayers. Table 2 shows the large decrease in R_{ct} of a $C_{16}SH$-coated Au electrode that occurs after scanning the electrode potential to extreme values. In these experiments we first measured R_{ct} using ac-impedance analysis, then we measured cyclic voltammetry between 1000 and -500 mV at a rate of 50 mV/sec and repeated the R_{ct}

measurement. Two potential sweeps reduced R_{ct} of the $C_{16}SH$-coated Au electrode by a factor of 140 while the R_{ct} of the 3-PAA/F- and 3-PAA/2F-coated electrodes decreased by factors of only 4 and 2, respectively. Increasing the number of potential sweeps (up to 10) removes the $C_{16}SH$ film from the Au substrate but has no measurable effect on the R_{ct} of 3-PAA/F- and 3-PAA/2F-coated electrodes. These results are consistent with other studies showing the reductive and oxidative desorption of thiols.[11,13-15,23,29] The excellent durability of the 3-PAA/F films makes them very attractive for corrosion inhibition applications.

Conclusions

The extent of surface passivation by 3-PAA films and their derivatives increases in the order 3-PAA<3-PAA/2F<3-PAA/F. Cyclic voltammetry and ac-impedance measurements show that the fluorinated films provide effective barriers to redox reactions. Any remaining electron transfer occurring at the electrode surface take place at an assembly of microelectrodes as shown by cyclic voltammetry. Although 3-PAA/2F films contain larger quantities of perfluoroalkanes and have higher contact angles than PAA/F films, blocking decreases slightly upon a second fluorination. This is likely due to a change in film morphology. Unlike organomercaptan SAMs, fluorinated PAA films are stable to potential cycling over a 1.5 V range. The durability and blocking characteristics, of fluorinated PAA films makes them attractive for corrosion inhibition. Additionally, the layer-by-

layer grafting of PAA films on SAMs provides good adhesion to the substrate as well as control over film thickness and composition.

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Table 1. Average charge-transfer resistances (R_{ct}), apparent surface coverages (θ) and active area $(1-\theta)$ of naked Au and Au coated with MUA, 3-PAA, 3-PAA/F, and 3-PAA/2F films in 5 mM $Fe(CN)_6^{3-/4-}$ (pH = 9.9, 1.0 M KCl).

Electrode	Film Thickness (Å)	R_{ct} ($\Omega \cdot cm^2$)	θ	$1-\theta$
Au	0	1.11±0.03[a]	0	1
Au/MUA	13	4.2±0.9[a]	0.74	0.26
Au/3-PAA	300	1.9±0.6 X 10^{3}[b]	0.99942	5.8 X 10^{-4}
Au/3-PAA/F	600	80±50 X 10^{3}[b]	0.999986	1.4 X 10^{-5}
Au/3-PAA/2F	700	26±11 X 10^{3}[b]	0.999957	4.3 X 10^{-5}

[a]R_{ct} was obtained by fitting the data to Randle's equivalent circuit using ZSIM software. The solution resistance was 60 Ω.
[b]R_{ct} was obtained using ZPLOT software to fit the semicircle at high frequencies.

Table 2. Charge-transfer resistance[a] and surface coverage of $C_{16}SH$, 3-PAA/F, and 3-PAA/2F films before and after cyclic potential sweeps.

number of potential sweeps[b]	$C_{16}SH$		3-PAA/F		3-PAA/2F	
	R_{ct} $(\Omega \cdot cm^2)$	$1-\theta$	R_{ct} $(\Omega \cdot cm^2)$	$1-\theta$	R_{ct} $(\Omega \cdot cm^2)$	$1-\theta$
0	5.3 k	2.0×10^{-4}	47 k	2.0×10^{-5}	21 k	5.0×10^{-5}
2	37	2.9×10^{-2}	12 k	9.0×10^{-5}	9.1 k	1.2×10^{-4}
4	4.3	0.25	11 k	1.0×10^{-5}	9.5 k	1.2×10^{-4}
10	1.1	1.0	11 k	1.0×10^{-5}	9.2 k	1.2×10^{-4}

[a]R_{ct} was determined using ac impedance measurements as described in the experimental section and the data come from one representative film.

[b]The potential is swept from 1000 to -500 mV (vs. Ag/AgCl, scan rate of 50 mV/s) in 5 mM $Fe(CN)_6{}^{3-}$ (pH = 9.9, 1.0 M KCl). Before and after the potential sweeps, the electrode was rinsed in 18 $M\Omega \cdot cm$ water.

Figure Captions

Figure 1. FTIR-ERS spectra of a 3-layer PAA film before fluorination (3-PAA) and after one (3-PAA/F) and two (3-PAA/2F) cycles of activation with ethyl chloroformate and reaction with $H_2NCH_2(CF_2)_6CF_3$.

Figure 2. Plots of complex impedance at many frequencies (Hz) for nominally naked Au and 3-PAA-, 3-PAA/F-, and 3-PAA/2F-coated Au electrodes in a pH 9.9-buffered aqueous solution containing 5 mM $Fe(CN)_6^{3-}$ and 5 mM $Fe(CN)_6^{4-}$.

Figure 3. Cyclic voltammetry of nominally naked Au (open squares) and MUA- (+), 3-PAA- (filled circles), 3-PAA/F- (x), and 3-PAA/2F- (solid line) coated Au electrodes in a pH 9.9-buffered aqueous solution containing 5 mM $Fe(CN)_6^{3-}$. The 50 mV/s frame also shows cyclic voltammetry of a $C_{16}SH-$ coated Au electrode for comparison (open circles).
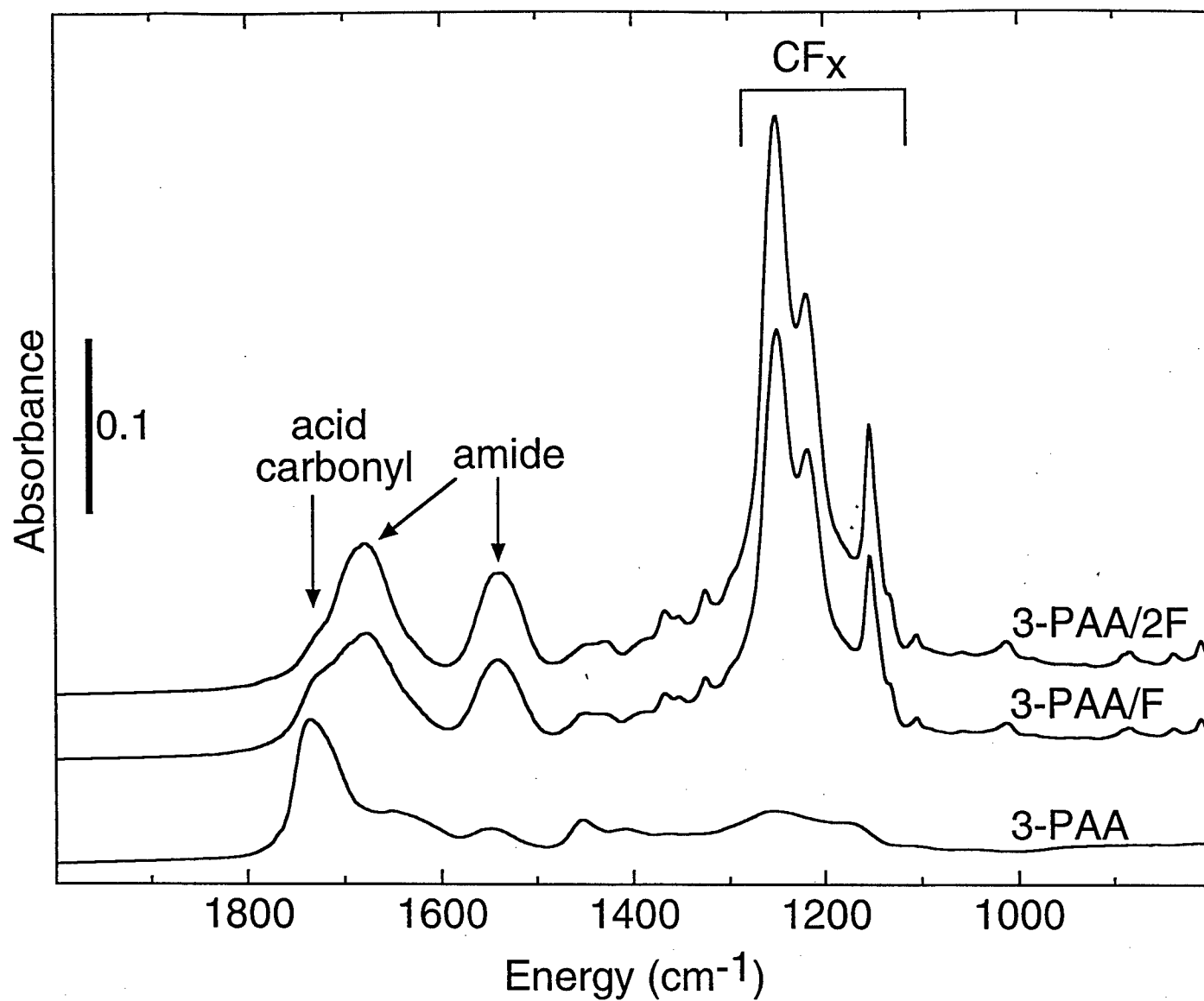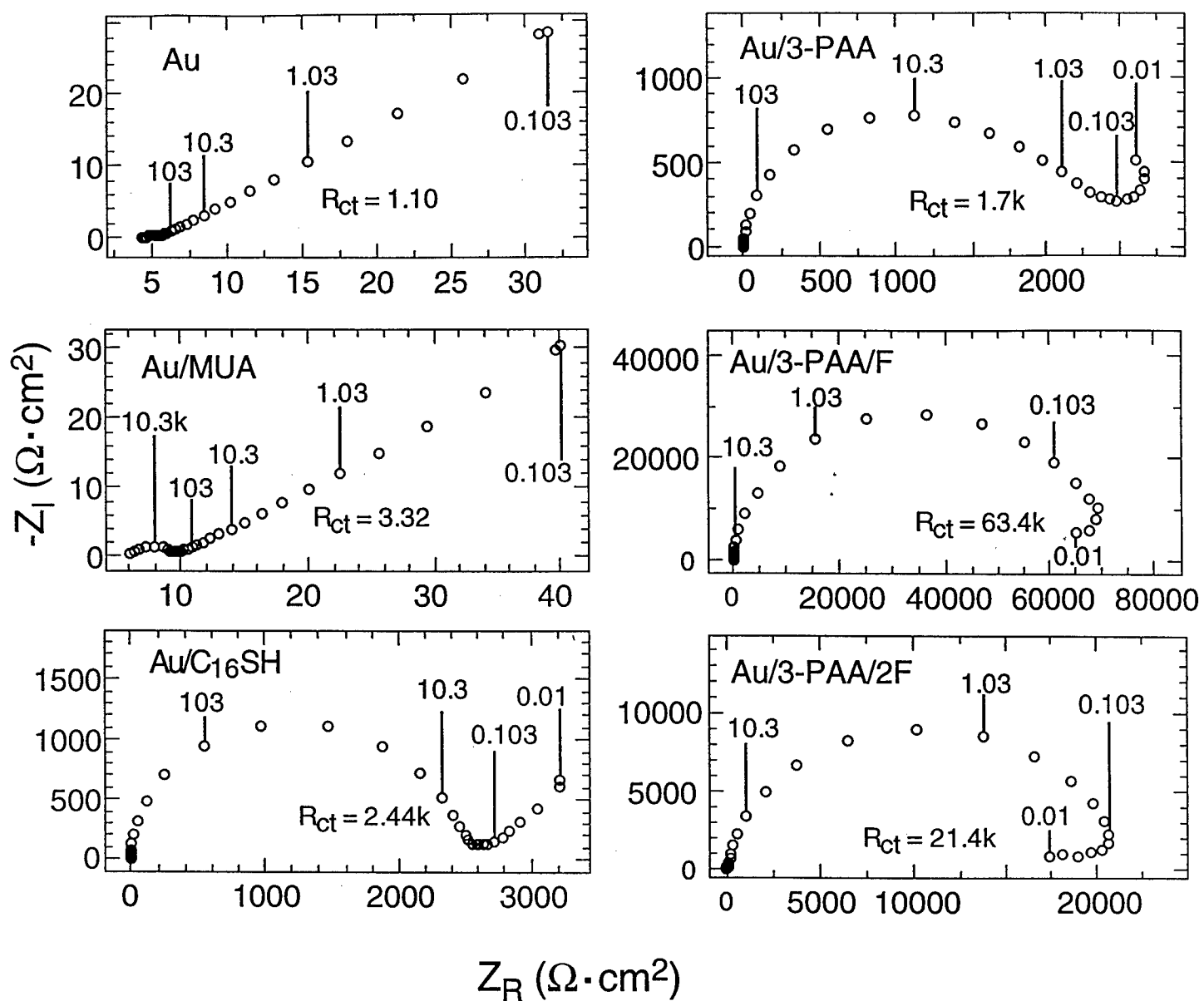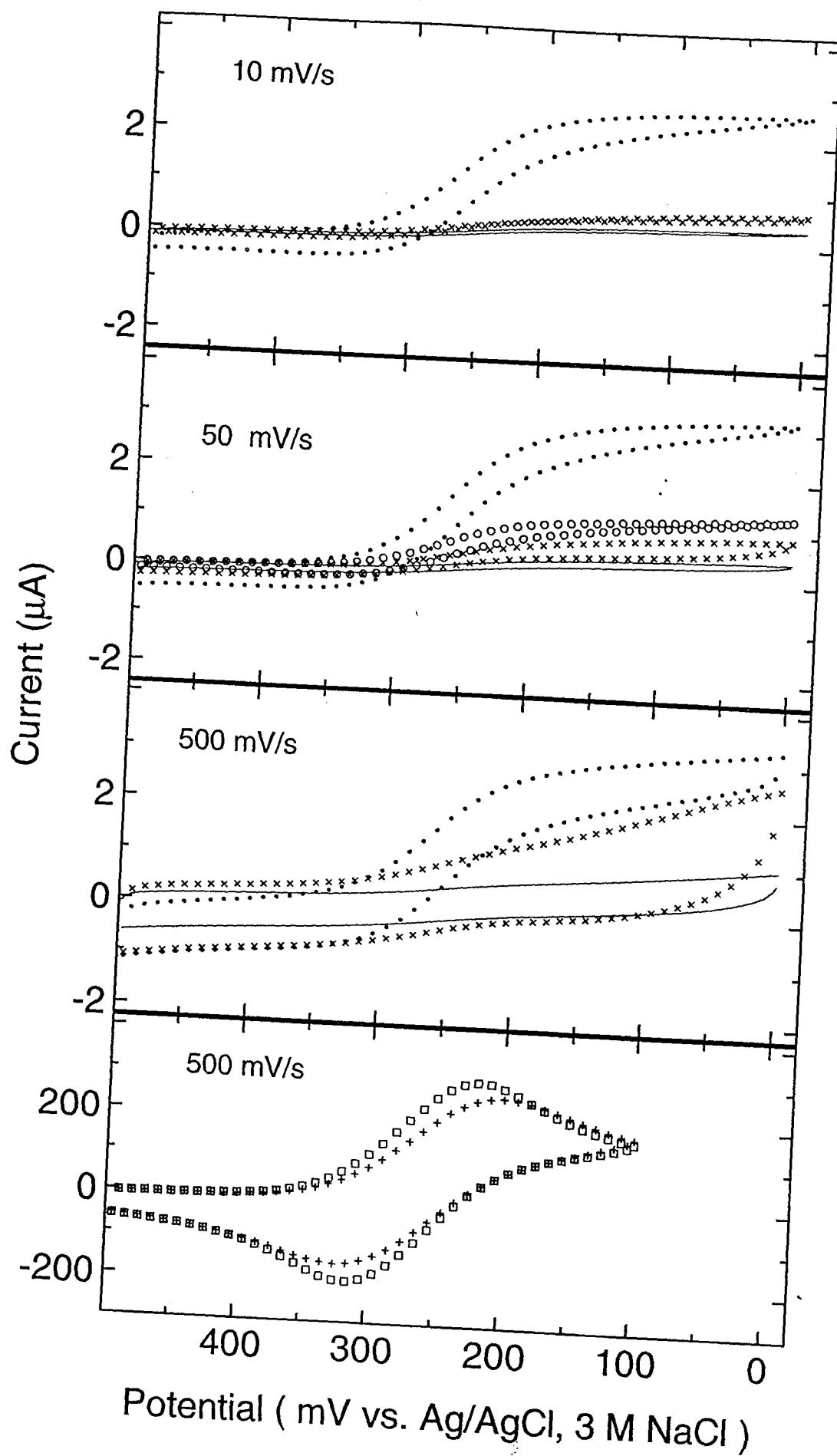
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